

Mechanism of polyphosphazene like film formation on InP in liquid ammonia (218 K).

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High electron saturation velocity and high thermal conductivity make InP a good candidate for metal-insulator-semiconductor transistors (MIS) [1]. However, the devices based on InP suffer from erratic electrical instability essentially due to the chemical interface evolution (e.g. oxides). In aqueous solution, using anodic treatments, the oxide growth on InP surface has been therefore explored to minimize those instabilities and increase device performances [2]. To minimize the density of traps at the insulator/InP interface, other wet processes have been investigated using for instance, inorganic sulfite chemistry [3,4], ruthenium deposition [5]. Nevertheless, a degradation of the surface network was rapidly observed. The air ageing of the InP surface leads inescapably to the loss of the expected electrical properties [6, 7].

The use of non aqueous solvents provides a large potential window to the electrochemical response of semiconductors. According to the nature of the solvent (physical and chemical properties), anodic treatments should strongly differ from aqueous media. The passivation treatment in non aqueous solvent seems to be a relevant option to avoid the formation of oxides surface. In past decades, many electrochemical processes have been studied in non aqueous solvents but electrochemical reactions are ruled by moisture, i. e. water chemistry (see e. g. [8]). Due to the high electronic purity of the solvent, liquid ammonia (NH₃ liq) has found a distinguished place in electrochemical studies of semiconductors. In liquid ammonia, the electrochemical formation of a monolayer phosphazene like film on InP was recently published [9-11].

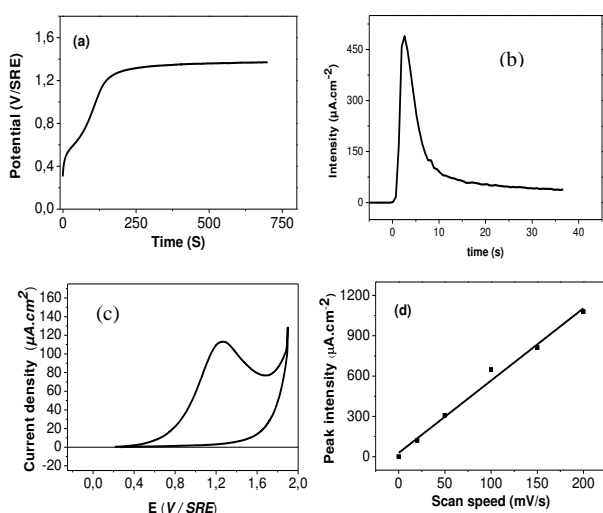


Fig.1: Electrochemical treatments on InP in liquid ammonia (218K): galvanostatic mode (a), potentiostatic mode (b), cyclic voltammetry (c), Evolution of peak intensity as function of scan speed (d).

The perfect coverage of the InP matrix by this nitrogenated film is revealed by electrochemical experiments and XPS data. In open air, no degradation of the thin film was evidenced by XPS, photo-luminescence and electrochemistry [12]. The high chemical stability of the phosphazene like film opens a new way for III-V semiconductors integration in electronic devices.

In this paper, the mechanism of the anodic process is explored using three electrochemical treatments (cyclic voltammetry, chronoamperometry, potentiometry). For each technique and according the anodic charge, a gradual evolution of the chemical surface is carried on by XPS analyses. The same ultra thin polyphosphazene like film is obtained whatever the electrochemical process used. For a total coverage surface and according the techniques, the atomic surface ratios are reported in the figure 2.

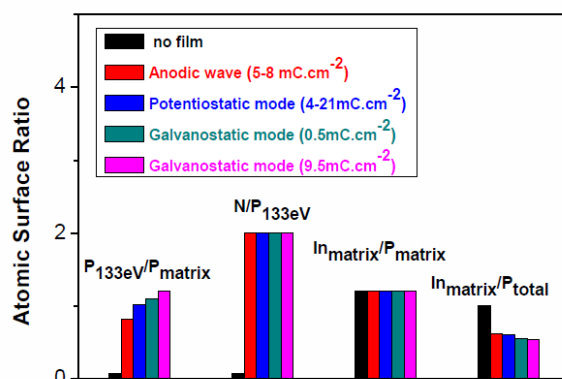


Fig. 2: Evolution of Atomic surface ratio after different electrochemical treatments.

In order to understand the electrochemical mechanism, a depth discussion on each technique is detailed. The limitation of the current is studied as a function of diffusion or adsorption phenomena. As well the cyclic voltammetry as the potentiostatic mode reveal an adsorption limitation step. After the full formation of the ultra thin film, the anodic charge is compared according the techniques. A drastic excess of charge is revealed for the potentiostatic and cyclic voltammetry mode. The comparison of the anodic charge raises a discussion on the faraday efficiencies. An electrochemical contribution of ammonia oxidation is evidenced in this work. The polyphosphazene like film formation on InP required the electrochemical oxidation of ammonia as a determinant step of the mechanism.

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